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First principles study of the Young's modulus of Si $\langle 001 \rangle$ nanowires

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We report the results of first-principles calculations of the Young's modulus and other mechanical properties of hydrogen-passivated Si $\langle 001 \rangle$ nanowires. The nanowires are taken to have predominantly $\{100\}$ surfaces, with small $\{110\}$ facets according to the Wulff shape. The Young's modulus, the equilibrium length and the constrained residual stress of a series of prismatic beams of differing sizes is found to have a size dependence that scales like the surface area to volume ratio for all but the smallest beam. The results are compared with two different models (and the results of classical atomistic calculations based on an empirical potential). We discuss the physics of the hydrogen interactions on the surface and the charge density variations within the beam that may account for the discrepancies of the models and the first principles results.

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Structures at the nanometer scale have drawn attention in recent years from various fields due to their anomalous mechanical, electronic, and optical properties as well as the advantages from their extremely small feature size[1–4]. Devices made of silicon or silicon oxide are of particular interest for technological applications. Quartz resonators and silicon resonators have been studied both theoretically and experimentally to gain higher performance[5–7], and one of the key material properties that determine the performance of a resonator is the Young's modulus. The Young's modulus is one of the intrinsic mechanical properties of any material: for macroscopic systems it is a material constant, independent of size. As the structure size of interest shrinks down to the nanometer scale, however, surface effects play an increasingly important role and the Young's modulus becomes size dependent. There has been study on quartz nanowires along this direction, but little has been done from first principles for equally important silicon-based nano-electro-mechanical-systems (NEMS), or silicon nanowires (SiNW's).

The challenge is that the silicon nanowires are governed by mixed physics: the small-scale physics, from confinement effects due to the reduced dimensionality to substantial surface effects due to the high surface-to-volume ratio, plays an important role, but at the same time, inside atoms feel the bulk-like environment. This leads to the practical difficulty in modeling a realistic system and interpret the outcome from such a model. Fortunately, there has been huge experimental effort along this direction, and it is of particular use to the systems found in experiments: one of the commonly encountered SiNW's is hydrogen-passivated wires. Hydrogen passivation is a natural residue after oxide rinsing with HF, and it is a good starting point for the surface condition of the wire[8]. As the surface effect dominates the mechanics, the surface condition is of great importance and may change not only the electronic properties but also the mechanical properties of SiNW's. In this study, all

the dangling bonds are perfectly passivated with a hydrogen atom and Si atoms on (001) facets will form symmetric dihydrides, i.e. two Si-H bonds sharing a single Si atom. Energetically canted dihydrides on the (001) surface lower the surface energy, but they are unlikely neither to change the nature of chemical bonding nor to significantly modify the Young's modulus of SiNW's. The consequence of symmetrization is discussed. For the atomic arrangement of inside Si atoms, single crystalline lattice is a reasonable approach in that single crystalline wires can be easily made in this size regime[6, 7], and in that this can provide the reference framework for possible extensions including defects. In this Letter, we report the complicated interplay between different kinds of physics associated with SiNW's with the emphasis on the size effect.

The first principles density functional theory (DFT) has been employed for this work. Specifically, the Vienna Ab-initio Simulation Package has been used along with projector augmented wave pseudopotentials[9, 10] within generalized gradient approximation (GGA) [11]. The energy cutoff for plane wave expansion is 29.4 Ry and higher, and 6 points in the one-dimensional irreducible Brillouin zone are used for k-point sampling. Each supercell is periodic in the wire growth direction, and has 10Å or more vacuum space in the transverse direction.

From the electronic structure's point of view, SiNW's are thought of as one dimensional structures: sensible evidence includes band gap increase due to quantum confinement[12, 13] and band dispersion change due to reduced dimensionality, i.e. switch from an indirect band gap to a direct band gap [14, 15]. On the other hand, they can be thought of as a three dimensional structures from mechanics' point of view, which have finite volume and hence the cross-sectional area. The entangled dual dimensionality is major challenge in any nanoscale mechanics study, in which continuum definitions of system variables such as cross-sectional area are obsolete.

The Young's modulus is, in principle, a stress-strain

TABLE I: Polynomial fittings of the Young's modulus of 57Si 36H. 10 data points are used for the fitting. Moduli in GPa.

Cutoff energy (Ry)	Order of polynomial fitting				
	2nd	3rd	4th	5th	6th
29.34	103.41	103.40	104.72	104.77	103.03
44.10	103.93	103.90	105.36	105.28	103.48
51.45	104.05	104.03	105.31	105.26	103.61

relationship, and the definition of stress and hence the cross-sectional area must be defined first. The definition of the cross-sectional area of a system of particles may not be defined uniquely, but in this work, it is defined without loss of generality as the area bounded by hydrogen atoms. The system volume (or any spatial dimensions) is determined from electron interaction rather than nucleus interaction although the mass of the system is condensed in the nuclei. For example, the lattice constant is determined by the point where the kinetic repulsion and the cohesive attraction balance out. In much the same way, the thickness of a metallic surface slab without explicit reconstruction could be determined by measuring the minimum energy separation of two identical surface slabs. This approach has been applied to the hydrogen-passivated surface slabs[16], but it remains questionable whether the same can directly be applied to nanowires or not considering that large separation within GGA (5 Å or 2.5 Å added to the thickness of the slab on each side) has been observed, and that the adsorbate-induced repulsion, not the intrinsic interaction between Si nanowires, is the source of such large separation. Still our definition is reasonable in the sense that most of electron density is enclosed by the boundary formed by hydrogen atoms and the electron density from Si atoms would almost vanish beyond this boundary.

The cross-sectional shape is a truncated square with 4 (001) facets and 4 (011) facets to avoid an unstable edge formed by two (001) facets. Due to the small scale and single crystalline structure, the cross-section can not be arbitrarily scaled. Rather, it has to commensurate with the underlying diamond-cubic lattice, and consequently there is a slight variation in the aspect ratio across the size, i.e. the shape effect and the size effect have not been completely deconvoluted. Nevertheless, this variation gives more number of data points and turns out to predict a clearer trend.

Based on the new definition of cross-sectional area, the Young's modulus of 57Si 36H wire has been calculated and tabulated in Table I. The Young's modulus is a second derivative of the strain energy with respect to the applied strain, and has been taken from the second order coefficient of the polynomial fit regardless the highest order of the fit. For the given order of fit, a higher cutoff energy hardly improves the fit, and for the given cutoff

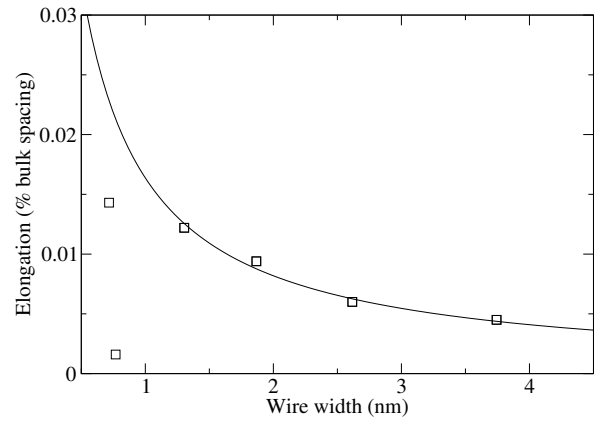


FIG. 1: Equilibrium length of hydrogen-passivated SiNW as a function of wire size. Solid curve is a $1/r$ fit to 4 data points from 1 nm or bigger wires.

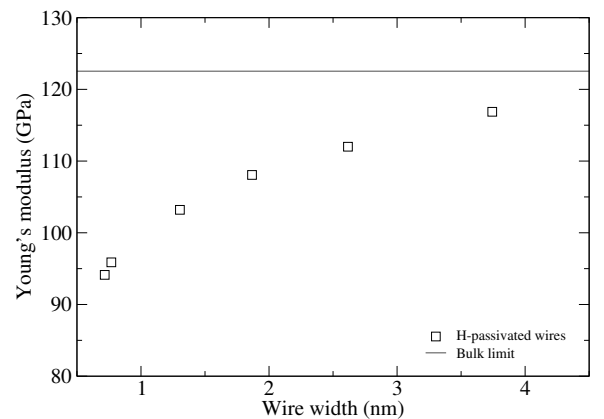


FIG. 2: Young's modulus of hydrogen-passivated SiNW as a function of wire size.

energy, uncertainty remains even if a higher order fit is employed. Considering that a higher order fit is more sensitive to any numerical errors in the calculations and only a limited number of data with finite accuracy is accessible due to high computational cost, a higher order fit is not always preferred. Moreover, the second order fit with 29.34 Ry energy cutoff seems reasonably good given that the error introduced in doing so is less than 2% compared with all the combinations tested. This also ensures the direct comparison with bigger wires where the number of data points and the energy cut off are essentially limited by the system size.

The equilibrium structure is determined from the balance between several competing effects. The intrinsic surface effect, in spite of the huge free surface area compared to the volume of the system, hardly introduces the surface stress, and the equilibrium length essentially remains unchanged. This is clearly seen in the case of the 25Si 20H wire in which the extrinsic surface stress due to H-H repulsion is almost negligible, and the result-

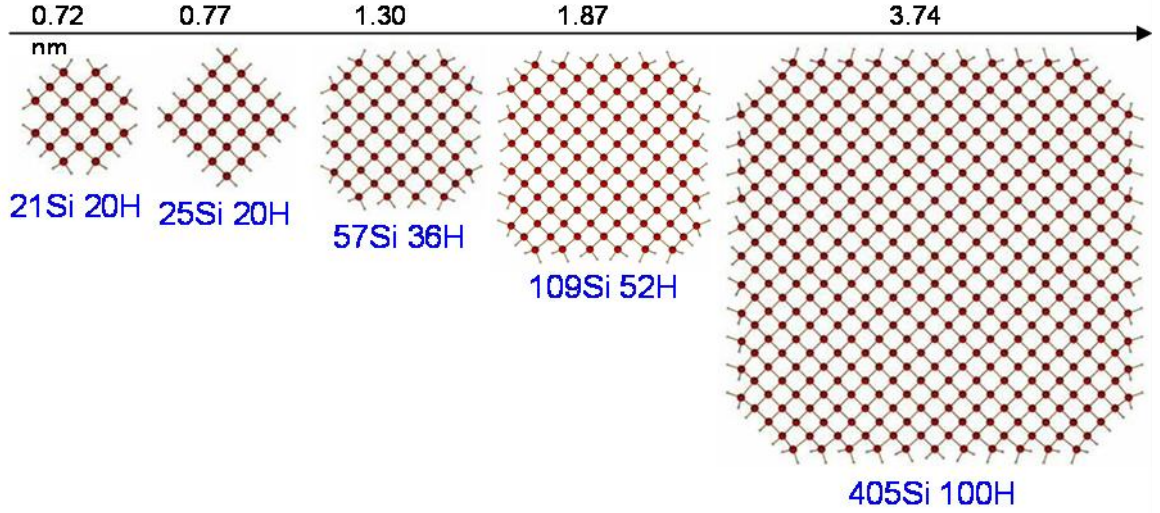


FIG. 3: Cross-section of fully relaxed hydrogen-passivated wires. The numbers represent the number of each species in the super cell. For example, 405Si 100H means that the super cell contains 405 Si atoms and 100 H atoms.

ing elongation is less than 0.002%. On the other hand, the extrinsic surface effect due to the hydrogenated surface layer plays a crucial role in changing the equilibrium length of the wires. Unlike the atoms on the (110) facets, which have one Si-H bond, the atoms on the (100) facets have two Si-H bonds and form a dihydride. The dihydrides on the (001) facets are aligned with symmetry such that two neighboring hydrogen atoms from adjacent dihydrides repel each other. (may refer to hydrogen molecule articles for the origin of repulsion) Since the dihydrides are aligned diagonally, the resulting repulsion introduces axial stress as well as transverse shear stress on the surface. The induced axial stress substantially stretches the wire, and the ground state length of the SiNW's with symmetric dihydrides tends to be longer than the bulk lattice spacing. Naturally, the bulk elasticity comes into play and counterbalances the elongation, trying to bring the wire length back to the bulk spacing. Consequently, the ground state length is determined from the balance between the surface stretching and the bulk restoring, or the surface-to-volume ratio, and hence, would ideally follow the $1/r$ dependence.

Other effects, however, add subtlety to the force balance and alter the $1/r$ dependence especially for the smaller wires. Nanowires are not perfectly continuous, and some may have the same aspect ratio while some others may not. Different aspect ratios mean different surface-to-volume ratios, and mean the change in the size-equilibrium length relationship. For example, 109Si 52H and 405Si 100H, having the same aspect ratio, are likely to fit in a single $1/r$ curve, while 57Si 36H and 205Si fit in another $1/r$ curve. Also important is the edge effect in that dihydrides on the edge are substantially relaxed

and exhibit weaker repulsion. The edge effect is more severe for small wires because the 21Si 20H wire, for example, has 2 surface atoms on each (001) facet, and essentially all the (001) atoms undergo substantial relaxation. On the other hand, a smaller fraction of (001) atoms are relaxed for the 405Si 100H wire. There are two more effects that play a role in the force equilibrium. First, the bulk anharmonicity appears as the wire is stretched beyond the limit of linear elasticity[17]; nevertheless it is few percent increase in the bulk stiffness for the strain range mentioned here, and hence not significant. Second effect is the H-H repulsion in the transverse direction on the surface. The more wires are elongated, the greater becomes the Poisson effect. In other words, elongation stretches the wire, but at the same time, shrinks the cross-sectional area, which, in turn, increases the repulsion between the dihydrides on the (001) facets because they are aligned diagonally. The transverse repulsion is clearly observed in the form of shear deformation.

The same level of complexity is observed for the Young's modulus as in the case of the equilibrium structure, but the impact of each contribution is different. First of all, the intrinsic surface effect plays a critical role in softening nanowires. Surface atoms, having less than 4 Si-Si bonds, can be regarded as having a smaller number of springs, and consequently soften the wire under uniaxial tension. This is clearly seen in the case of the 25Si 20H wire: even though any extrinsic surface effect is negligible, i.e. the ground state length almost remains at the bulk lattice spacing, the soft surface layer diminishes the material stiffness with the given high surface-to-volume ratio. Evidently, the covalent nature of bonding is preserved even with a high surface-to-volume ratio, and a

simple bond-counting argument holds. The local environment of surface atoms is virtually similar to the bulk environment even though a Friedel-like oscillation, due to the surface relaxation and the natural structure of silane chains, is present. This is a different situation from a metallic surface where significant charge redistribution occurs.

The complexity arises from the general belief that the compressive stress is related to the material stiffening, while the SiNW's soften as the size shrinks even though the equilibrium length increases as can be seen in Fig. 2. This common belief, however, is not entirely true because it is the surface elastic constant (or strain-derivative of the surface stress), not the surface stress evaluated at the bulk equilibrium (or simply surface stress), that changes the net stiffness[18]. Therefore, a wire with compressive surface stress could result both in softening and stiffening depending on the sign of the surface elastic constant. Another reason for the complexity of underlying nanomechanics is the mixture of intrinsic and extrinsic surface effects. Only the extrinsic effects stands out for the surface stress, but for the material stiffness, the intrinsic effect dominates.

It turns out that the extrinsic surface effect plays a secondary role in the stiffness change, but the impact is not as big as that from the intrinsic effect. Due to the exponential nature of the repulsive force, the H-H tend to stiffen the compressive domain but soften the tensile domain, resulting in noticeable anharmonicity. Interestingly, such anharmonicity observed in the calculations of surface slabs is not observed in the case of nanowires. This can be explained with the Poisson effect as is the case with the equilibrium length. As a wire is elongated, the longitudinal repulsive force exponentially decreases but the transverse repulsive force exponentially increases. Two competing driving forces tend to balance at some point where two opposite anharmonic effects cancel out.

Another impact that the substantial elongation by the H-H repulsion brings in is the effect of bulk anharmonicity. The bulk anharmonicity increases the Young's modulus when the applied tensile strain is beyond the range of linear elasticity. Nevertheless, the bulk anharmonicity due to the stretch contributes little to the net material stiffness. Based on the 5th order polynomial fit of bulk uniaxial tension data, the bulk anharmonic stiffening for the smallest wire is less than 2%.

In conclusion we have found that calculation of several mechanical properties of silicon nanowires from first principles reveals a size dependence in properties that would be size-independent constants for macroscopic systems: the equilibrium length and the Young's modulus. Another property, the residual stress in a beam constrained at the bulk equilibrium length, is zero for a macroscopic beam, and in nanowires it is non-zero and size depen-

dent. In each of these cases the size dependence scales roughly as the surface area to volume ratio. In the case of the hydrogen terminated surfaces studied here, the effect is not strong. For example, the Young's modulus is softened by about 20% for a 1 nm diameter wire. Since the resonant frequency of a flexural resonator depends on its Young's modulus, it may be possible to measure this effect directly.

Another interesting possibility is that the effect could be substantially stronger in silicon nanowires with different surfaces, such as bare surfaces or oxide surfaces. These systems are more challenging for first-principles calculation due to a greater number of candidate structures and a greater role for charge transfer in the mechanics. It is not clear whether the Young's modulus would increase or decrease as the size of the beam is reduced. There is much to be learned still.

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